

**APPENDIX****RESPONSE TO ARGUMENTS OF THE EXAMINER'S OFFICE ACTION OF  
AUGUST 8<sup>th</sup>, 2007****Serial No. 10/518,443****Examiner's Argument**

Applicants argue that the reference relied upon by the examiner use an electron donor, which is a Lewis base because it has lone pairs of electrons that it can donate, and that since titanium is a Lewis acid that the titanium catalyst will be poisoned by any Lewis base, which are compounds with oxygen, as defined by the applicants. This however, is found not persuasive because applicants composition uses silica for a support, which clearly also has oxygen atoms that would act as a Lewis base and poison applicants Lewis acid catalyst, in the same way that Lewis bases would poison that catalyst of the references, based on this line of reasoning either applicants argument is flatly incorrect or applicants catalyst will not work because it too is poisoned.

**Applicants' Response**

The oxides of non-metals, such as SiO<sub>2</sub> or silica gel, are examples of inorganic solid supports very used in the field of the chromatography and of catalytic reactions, where the chemistry of the surface plays a predominant role. The chemistry of the surface of the silica is, to a large extent, dominated by hydroxyl groups or silanol groups (Si-O-H). The subject of surface silanols has been studied extensively over the past seven decades and has been reviewed (see refs. 1-5). To explicitly define the surface of these composites, it is necessary to determine the number of such groups, their dissociation behavior and the nature of their interaction with the components of the surrounding medium. The literature contains a large amount of infra-red spectroscopic data on these oxides (see refs. 6-8). This technique has been successfully used, combined with others techniques (such as <sup>29</sup>Si solid NMR, for instance), to differentiate the hydroxyl groups in different environments. Interaction with specific adsorbates gives a measure of the type of bonding in which the hydroxyl groups may be involved, and also provides information on the acidity of the surface in terms of Lewis and Brönsted sites.

As described before, the surface of silica gel consists of hydroxyl or silanol groups and physically adsorbed water. Most of the water is removed upon drying in air at 400-500 K. Silanol groups are left on the surface and exist in three different configurations, i.e. isolated (a), geminal (b) and vicinal (c) (see ref. 9). These three basic types of silanol are shown in Figure 1.

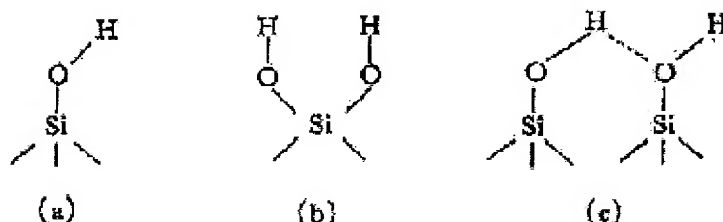


Figure 1

Hydrogen-bonded hydroxyl groups condense to strained siloxane groups, which act as Lewis basic sites, as shown below (see ref. 10):

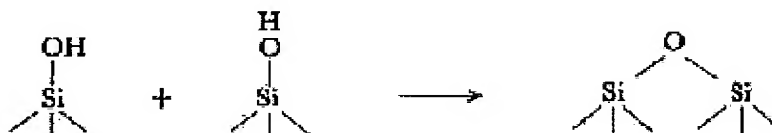


Figure 2

The usual way to control the concentration and strength of these silanol groups is through the pretreatment of the support, mainly by calcination at different temperatures (see ref. 11).

The chemical nature of silica has been studied by diverse researchers. In accordance with Schindler and Kamber (see ref. 12), Strazhesko *et al.* (see ref. 13) and Hair and Hertl (see ref. 14), the silanol groups are of acid nature. According to the Brönsted-Lowry (see ref. 15) and Lewis (see ref. 16) definitions, a solid acid shows a tendency to donate a proton or to accept an electron pair, respectively. One of the methods used for determination of this acid nature is titration of these groups with various bases, determining their  $pK_a$ -values. As for example, the acidity of silica was determined by the irreversible adsorption of pyridine ( $pK_a = 5.25$ ) giving the value of 0.206 mmol/g, while aniline ( $pK_a = 4.6$ ) gave the value of 0.01 mmol/g. Another evidence of the Brönsted or Lewis acidity of silanol groups, was demonstrated by authors as Hair (see ref. 7) and Kiselev and Lygin (see ref. 17), in infra-red

spectroscopic studies where the direct involvement of these groups with a large variety of adsorbate molecules were determined (See Table 1).

Table 1

**Table 6.1. Frequency shift (lowering from 3750  $\text{cm}^{-1}$ ) by adsorption on silicas**

Adsorbate	$\Delta\nu$ (Lowered, $\text{cm}^{-1}$ )	Adsorbate	$\Delta\nu$ (Lowered, $\text{cm}^{-1}$ )
Ar	8	Benzene	110
O <sub>2</sub>	12	Toluene	130
N <sub>2</sub>	24	Aniline	550
CH <sub>4</sub>	32	Phenol	350
NH <sub>3</sub>	800	Nitrobenzene	140
CO	130	<i>n</i> -Hexane	50
CH <sub>3</sub> OH	330	(CH <sub>3</sub> ) <sub>3</sub> COH	435
CCl <sub>4</sub>	40	C <sub>5</sub> H <sub>5</sub> N	850
CH <sub>2</sub> Cl <sub>2</sub>	72	Thiophene	130
CH <sub>3</sub> Cl	140	CH <sub>2</sub> Cl-CH <sub>2</sub> Cl	140

The frequency shifts are donated by  $\Delta\nu$  ( $\text{cm}^{-1}$ ), lowered from 3750  $\text{cm}^{-1}$  (characteristic OH stretching vibrational frequency by infra-red frequency (see refs. 1, 7 and 17).

The literature data showed that the adsorbate molecules fall approximately into three classes in regard to strength of interaction with silanol groups (see ref. 1):

*Low:* Argon, N<sub>2</sub>, CCl<sub>4</sub>, n-alkanes, cyclohexane

*Medium:* CH<sub>3</sub>NO<sub>2</sub>, C<sub>6</sub>H<sub>6</sub>, CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub>, CH<sub>3</sub>CN, tetrahydrofuran, dioxane, acetone, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O

*Strong:* NH<sub>3</sub>, C<sub>5</sub>H<sub>5</sub>N, aniline, phenol, CH<sub>3</sub>OH

Hydrogen-bonding with silanol groups is involved for medium and strong interactions and this fact demonstrate the Brönsted-Lowry or Lewis acidity of these groups on silica (see ref. 18).

Other evidence of the acidity of silanol groups is shown by the interaction of commercial silica with solvents as benzene, dioxane and tetrahydrofuran (see ref. 19).

As commercial silica, used as catalytic supports, are usually thermally treated at temperatures that can reach 600-700°C, siloxane groups can appear, as mentioned previously. However, these groups which are Lewis base, appears in the surface of the silica in only 0.15 siloxane groups/nm<sup>2</sup> (see ref. 20). The number of silanol groups in

the surface of precipitated silica can vary from 4.5 OH groups/nm<sup>2</sup> (see ref. 1) up to 8-9 OH groups/nm<sup>2</sup> for Xerogel silica (see ref. 2).

Summarizing, the silanol groups of the silica are of acid nature (Lewis or Brönsted acid) and not basic. Although the existence of a free electron pair in the oxygen of silanol groups, the reactivity of these groups occurs through the hydrogen consumption. So, these OH groups cannot act as bases of Lewis poisoning the catalyst in contrast to organic molecules endowed with free electrons, as for example, tetrahydrofuran, ethanol, etc.

Another important point is that, in the case of our patent application, before the reaction of the thermal treated silica with Ti and Mg compounds, the remained silanol groups are reacted with aluminum alkyl (preferably, triethyl aluminum). The reaction, in this case, occurs between the hydrogen from silanol group and the alkyl group from, for example triethyl aluminum, generating the ethane gas as by-product. This fact was already demonstrated by other authors (see refs. 21-31). Consequently, the possibility of total poisoning of the catalyst does not exist, as mentioned by the Examiner.

#### **Examiner's Argument**

Applicants argue that no electron donor is used in their invention. This is found not persuasive because based on applicant's own admission Lewis bases are electron donors and since silica is a Lewis base it is also an electron donor.

#### **Applicants' Response**

See the response of the previous item.

#### **Examiner's Argument**

Applicants argue that an aluminum alkyl since it is a Lewis acid it can remove electron donors from Ti and MG site. This is not persuasive because: 1.) Applicants have shown no evidence that aluminum alkyls are stronger donors than Ti or Mg and can actually remove these groups from Ti and MG sites 2.) If aluminum alkyl are such powerful Lewis acids as applicants suggest, then the aluminum alkyls would be bound to all the free oxygen sites of the support, and not be available to remove these electron donating groups as applicants suggest, and applicants have provided no evidence to the contrary.

### Applicants' Response

The use of electron donors or Lewis bases on Ziegler-Natta catalyst type is of public domain, as it can be seen, for example, in references 32 – 34. Starting in 1969, a wide range of electron donors was tested in a systematic evaluation of their effectiveness (see refs. 33-34). The objective was to move the polymerization off of the normal relationship between activity and stereospecificity, where higher levels of stereospecificity could be achieved only at the expense of very low activities.

In order to increase stereospecificity, various types of electron donors were employed as additives in the solid catalyst (called “internal donor”) and also in the polymerization system (called “external donor”).

A number of papers have been published concerning the role of Lewis bases on polymerization (see refs. 35-36). Busico *et al.* proposed a plausible model for the active sites on the  $\text{MgCl}_2$  crystal surfaces (see figure 3). They also proposed that internal donor, ethyl benzoate, predominantly adsorbs on more acidic sites, the (110) faces, to prevent  $\text{TiCl}_4$  from forming non-stereospecific sites-III, while the external donor, ethyl benzoate, prevents the extraction of internal ethyl benzoate as well as deactivates the non-stereospecific site-I selectively (see ref. 37).

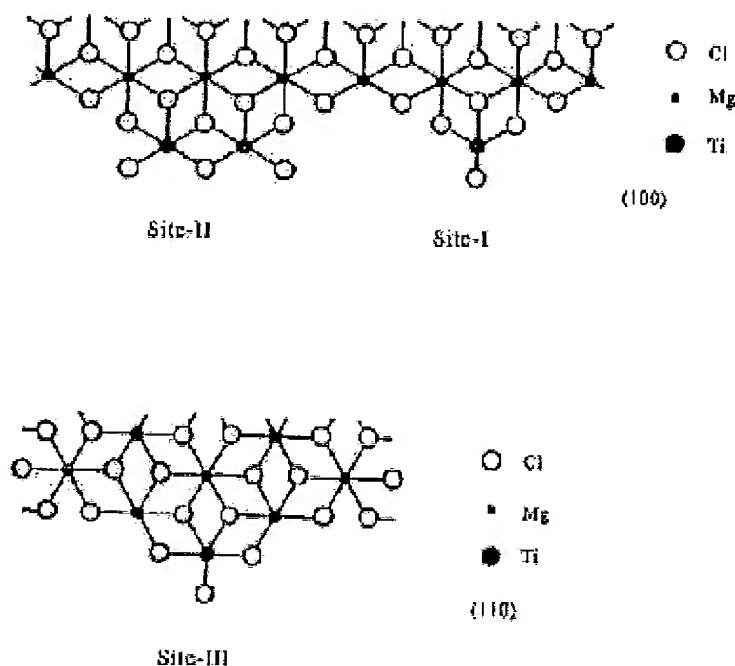


Figure 3

In a polymerization reaction involving  $\text{MgCl}_2$ -supported catalysts such as the Ziegler-Natta ones, it is important to add another component to activate this compound, which is the cocatalyst. The most used one are aluminum alkyl compounds like TEAL (triethyl aluminum) and TIBA (tri-isobutyl aluminum) (see ref. 33). Some electron donors used as internal donor, can suffer irreversible chemical reactions with these aluminum alkyls compounds.

Some literature has shown TEAL or TIBA interaction with, for example an aromatic monoester, whose chemistry was recently revised by several authors (see refs. 36, 38-40). According to these authors, the interaction involves the formation of an acid-base complex through the oxygen of carbonyl group. They use infra-red spectroscopic technique to show the chemical shift of stretching vibrational frequency of carbonyl, from  $1725\text{ cm}^{-1}$  (free ester) to  $1655\text{ cm}^{-1}$  and  $1670\text{ cm}^{-1}$ , correspondent to the aluminum alkyl/electron donor mixture. Structures demonstrating these interactions had been proposed by Spitz (see ref. 41), as shown in the figure 4:

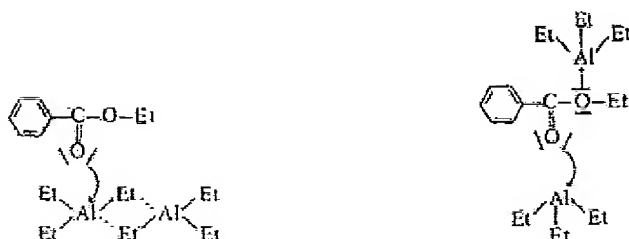


Figure 4

Another technique used by other authors to demonstrate the aluminum alkyl/electron donor interaction is the  $^{13}\text{C}$  NMR spectroscopy (see refs. 42-43).

These electron donors can undergo a further reaction, especially in the presence of excess of aluminum alkyl, as is usual for polymerization. In the case of aromatic monoester, such as ethyl benzoate, a nucleophilic attack of free aluminum alkyl on the carbonyl group complexed with aluminum alkyl has been postulated. The reaction leads finally to the formation of two moles of dialkylaluminumalkoxide per one mole of ester, according to the following figure 5 (see refs. 36, 44-45).

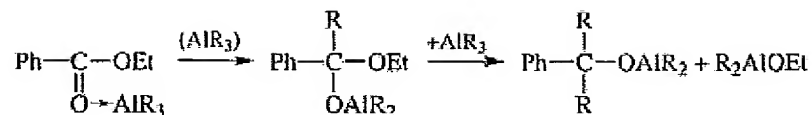


Figure 5

Summarizing, the aluminum alkyl can remove the electron donors from Ti and Mg sites, as demonstrated above.

In our Patent Application Serial No. 10/518,443, as mentioned before, the silanol groups from silica or the oxygen sites of the support, as reported by the Examiner, are reacted with aluminum alkyl (preferably, triethyl aluminum), as can be seen in step (a) from the Claim 48 of the Preliminary Amendment (from July 20, 2007). In such a case, this aluminum alkyl was used with the intention to react with the hydrogen from silanol groups preventing the Ti and Mg sites to be supported direct to these OH groups. However, during a polymerization reaction, aluminum alkyl is used to act as cocatalyst in a great amount and, as mentioned before, this excess reacts with electron donors from catalyst composition in a nucleophilic reaction (See figure 5). As can be seen in our Patent Application Serial No. 10/518,443, no electron donor is used, as demonstrated in Summary of the Invention, in Detailed Description and in Claims.

However, in patents EP 0522651 B1 and EP 0480435 B1, they use an electron donor as a solvent (ethyl acetate or ethyl benzoate, as examples) for the titanium and magnesium solution. The remaining electron donor at the final catalyst can be removed by this aluminum alkyl, as proved before.

### Examiner's Arguments

Applicants argue that since they use a lower amount of titanium they have better comonomer insertion. This is not persuasive because if having lower amounts of active titanium gives better results, then this would be expected to happen in a catalyst that has more titanium, but roughly the same number of active sites due to this supposed "poisoning" caused by the electron donor applicants talk of.

### Applicants' Response

This would be true if the electron donor used as solvent in step (a) of the patent EP 0480435 B1 or in step (ii) of the patent EP 0522651 B1 would not be removed by evaporation, as mentioned in step (c) of the patent EP 0480435 B1, or reacting with aluminum alkyl as mentioned in step (d) of the patent EP 0480435 B1 or in step (iii) of the patent EP 0522651 B1. Some authors, as can be seen below, have shown the effect of having the electron donor during ethylene copolymerization and the effect after the removal of these compounds. They also studied the effect of the titanium concentration on catalyst performance.

Sindelar *et al.* showed the effect of titanium concentration on silica supported catalysts on activity and polyethylene properties (see Figure 6 – Ref. 46). They observed an increase of activity with titanium concentration only up to 0.2 mmol Ti/g silica. Higher concentration of titanium only deteriorates the catalyst activity probably due to formation of Ti-Ti agglomerates. They also studied the effect of THF addition on activity, bulk density and melt index of the obtained polyethylene. It was observed activity enhance, while on the other hand it causes the deterioration of polymer parameters (see Figure 7).



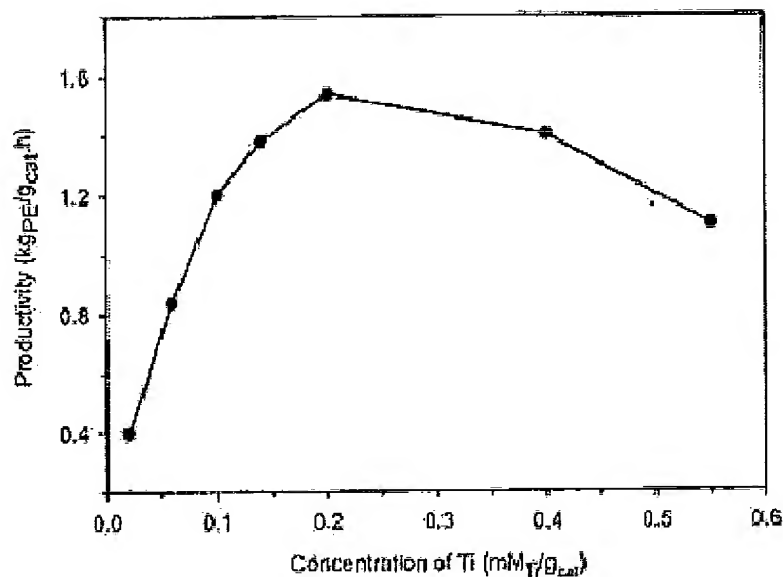


Figure 6

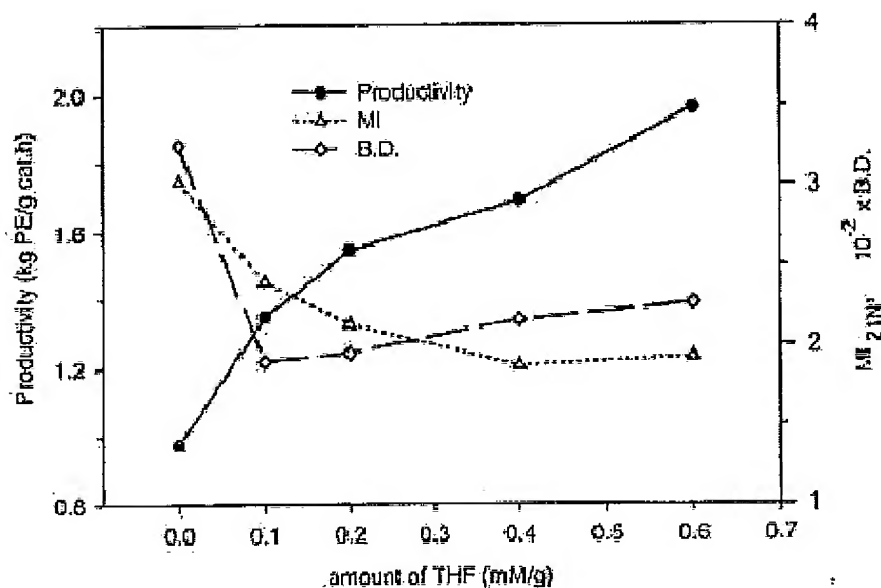


Figure 7

Chang *et al.* prepared titanium based catalysts with different amount of THF as electron donor and evaluated them through XRD and ESR spectroscopy. They studied the influence of different amount of this donor on  $Ti^{3+}$  species and as consequence, on ethylene-propylene copolymers microstructure and activity. The  $^{13}C$  NMR study showed that the microstructure of these copolymers strongly depended upon the nature of  $Ti^{3+}$ . It was also observed that the THF content affect the molecular weight

distribution of these copolymers, i.e. the molecular weight distribution became broader with THF removal (see ref. 47). Multinuclear  $\text{Ti}^{3+}$  species increased the relative reactivity of propylene in the copolymerization, and isolated  $\text{Ti}^{3+}$  species with vacancies favored random insertion or propylene in the ethylene main chain.

Mori *et al.* investigated the nature of titanium species from Ziegler-Natta catalysts prepared with different internal donors through X-ray photoelectron spectroscopy (XPS). They concluded that the internal donor existed free from titanium species on the supported catalysts, but the nature of the active sites was affected by the change in the environment through the interaction of the donor with  $\text{MgCl}_2$ . As can be seen on Table 2, Ziegler-Natta catalysts, with and without internal donors, showed Ti 2p<sub>3/2</sub> signal with the full width at half maximum intensity (FWHM) between 2.9 and 3.0 eV. It is important to say that FWHM represents the heterogeneity of titanium species: the larger the width of this signal, more heterogeneous is the species in those catalysts. After the treatment of these supported catalysts with TEAL, the FWHM increased, as can be seen in Figure 8 (see ref. 48).

Table 2

XPS data of the  $\text{Ti}_{2p_{3/2}}$  level in the supported catalysts and  $\text{TiCl}_4$ -ester complexes

Run No.	Catalyst	Binding energy <sup>a</sup> (eV)	FWHM <sup>b</sup> (eV)
1	$\text{TiCl}_4/\text{EB}/\text{MgCl}_2$	458.8	3.0
2	$\text{TiCl}_4/\text{DBP}/\text{MgCl}_2$	458.9	3.1
3	$\text{TiCl}_4/\text{MgCl}_2$	458.9	2.9
4	$\text{TiCl}_4 \cdot \text{EB}$ complex	459.1	2.4
5	$\text{TiCl}_4 \cdot \text{DBP}$ complex	459.2	2.4

<sup>a</sup>Reference:  $\text{Au}_{4f_{7/2}}$  (84.0 eV).

<sup>b</sup>Full width at half maximum intensity.

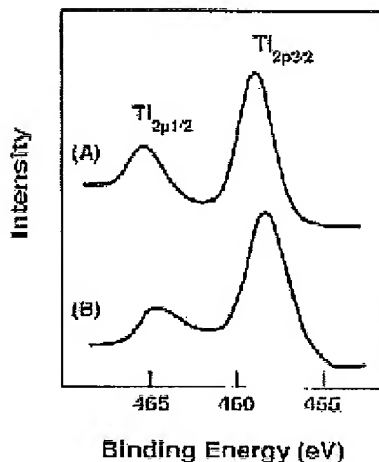


Fig. 2. XPS spectra of  $Ti_{2p}$  levels in  $TiCl_4/EB/MgCl_2$  (A) and the TEA-treated catalyst (B).

Figure 8

Examples 1 and 3 from the patents EP 0522651 B1 and EP 0480435 B1, respectively, were reproduced in our lab and analyzed by XPS and compared to catalyst Example 8 from our Patent Application Serial No. 10/518,443, as shown in Table 3. As all these examples use TEAL as cocatalyst during polymerization, we have analyzed them with and without the reaction with TEAL.

Table 3

Catalyst	TEAL Reaction	FWHM (eV)
Patent EP 0522651 B1 (Example 1)	No	2.5
	Yes	3.6
Patent EP 0480435 B1 (Example 3)	No	2.7
	Yes	3.5
Patent Application Serial No. 10/518,443 (Example 8)	No	3.0
	Yes	3.0

As previously mentioned and demonstrated by diverse authors (see refs. 36, 44-45), the use of excess of aluminum alkyl as cocatalyst in the polymerization reaction can remove most of the electron donors presented in the catalytic composition of the patents through a nucleophilic reaction (See figure 5). As a consequence, the effect of

“selective poisoning” can be reduced since of the electron donor can be also removed from catalytic composition through reaction with the cocatalyst (aluminum alkyl).

It can be seen in Table 3 that both catalysts from patents EP 0522651 B1 and EP 0480435 B1 show narrower FWHM (lower values) when compared to the Example 8 from Patent Application Serial No. 10/518,443. However, when all catalysts are put in contact with the cocatalyst (TEAL), FWHM become larger (higher values) for both catalysts from patents EP 0522651 B1 and EP 0480435 B1 and does not change for example 8 from Patent Application 10/518,443. The plausible explanation is the possible removal of any residual electron donor (from ester used on catalysts preparation) presented in examples of patents EP 0522651 B1 and EP 0480435 B1, which reduce the “selective poisoning” of active titanium sites.

Some commercial Ziegler-Natta catalysts show in their composition tetrahydrofuran as internal electron donor (see refs. 47 and 49) and this ligand can coordinate to titanium, magnesium and some exist as solvent of crystallization. Some analysis, as thermogravimetry, of such catalysts with THF in composition, show that most of this electron donor can be swept away in a nitrogen stream at 80°C over 2 h. DSC reveals strong heat absorption (evaporation) at the same temperature. These results suggest that desorbed THF is readsorbed in other adsorption sites on the catalyst. These two analytical procedures suggest that almost all THF is fairly mobile.

Summarizing, the electron donor removal from the catalyst leads to a higher heterogeneity of the sites, as already observed by several authors (see refs. 46-48).

### **Examiner's Arguments**

Applicants argue that in their invention aluminum alkyl can be used to remove any remaining electron donors from the Ti and Mg sites, however, if applicants desire to have aluminum alkyl as a co-catalyst, then there is the problem that no aluminum alkyl is left over to act as a co-catalyst once it is all bound up by Lewis bases, and applicant show no teaching to add enough aluminum alkyl to sequester the electron donor then add extra to act as a co-catalyst, and even if there was based on the logic from applicants own arguments there would still be no aluminum alkyl to act as a co-catalyst since it will be bound to the silica, which is a Lewis base.

### Applicants' Response

It is true that the aluminum alkyl can remove remaining electron donor left at catalyst composition, as mentioned before. At catalyst preparation, for the present Patent Application Serial No. 10/518,443, aluminum alkyl is used in step (a) from the Claim 48 of the first Preliminary Amendment (from July 20, 2007) to react with the hydrogen from silanol groups and optionally in step (i). In all three patents, EP 0522651 B1, EP 0480435 B1 and WO 91/08239, they also mentioned the use of these Lewis acids during catalyst preparation. Despite the use of the Lewis acids during catalyst preparation, it is common to use an excess of aluminum alkyl during polymerization and this cocatalyst has the following functions: catalyst's alkylation, oxidation state reduction of titanium species and reaction, as scavenger, with impurities from raw materials used in polymerization (solvents, monomers, nitrogen, etc.) (see ref. 32 and 33).

Summarizing, the aluminum alkyl used during catalyst preparation from the present Patent Application Serial No. 10/518,443, is used to react with silanol groups and, and during the polymerization, another amount of aluminum alkyl is used with the objective to activate the titanium species already in catalyst (catalyst's alkylation, oxidation state reduction of titanium species) and removal of impurities from polymerization raw materials (solvents, monomers, nitrogen, etc.).

### Examiner's Arguments

Applicants submit evidence in an attempt to show unexpected result, however, these results are not fully commensurate with the scope of the claims or the references. Furthermore, the properties that applicants try to use to show unexpected results are not limitations from the claims.

### Applicants' Response

In our last Response to Examiner (July 2007), we have shown results to compare the present Patent Application Serial No. 10/518,443 examples with some from the

patents EP 0522651 B1, EP 0480435 B1 and WO 91/08239, which were reproduced in our lab. We compared the Ti, Mg and Cl ranges from our present Patent Application Serial No. 10/518,443 and from EP 0522651 B1, EP 0480435 B1 and WO 91/08239 patents. We also compared copolymerization runs with some examples from our present Patent Application Serial No. 10/518,443 and from EP 0522651 B1, EP 0480435 B1 and WO 91/08239 patents. All parameters, regarding polymer properties as Bulk Density, MFI, Butene Content, Density and Xylene Soluble, shown in last Response to Examiner (July 2007), were described in Background Information, Summary of the Invention, Detailed Description and Claims from the present Patent Application Serial No. 10/518,443.

All results presented in our last Response to Examiner (July 2007) show that the polymer's properties are dependent on the chemical environment of active sites (see ref. 50).

#### **Examiner's Arguments**

Examiner notes that many of the amended claims have the limitation substantially free of polar solvent. Examiner would like to point out here that the reference of Luciani clearly teaches the removal of the ester solvent, which, would read on the instant claims.

#### **Applicants' Response**

We agree with the Examiner that the liquid ester of an aliphatic acid used as solvent in patent EP 0480435 B1 can be removed by evaporation from catalyst in step (c). However, as proved before by other authors, residual electron donor can be remained after thermal treatment (see refs. 49). Probably this electron donor, removed by thermal treatment, is that of solvent of crystallization. As already discussed, the other

electron coordinated to titanium and magnesium, demand higher energy for removing which can be achieved by chemical reaction with aluminum alkyl.

We would like to point out that as described in patent EP 0480435 B1, it is mentioned that total evaporation of the ester is not necessary and at the end of step (c) of this patent, it may still be present in quantities of up to 20% by weight, preferably no more than 5 to 10% by weight, with respect to the weight of the magnesium chloride (see from lines 21 to 24 from page 3).

#### **Examiner's Arguments**

Applicants argue against examiners earlier position that the instant claims only recited relative amounts, and have therefore, added the specific amounts. However, examiner would like to point applicants attention to page 2 of Luciani I in lines 25-28 it is taught that 50-90 wt % is silica and 10-50 wt % is made up of Ti, Mg, Cl, and alkoxy groups, then in lines 29-32 Luciani teaches that the Ti/Mg molar ratio can vary from 0.2-1 to 5-1, which if calculated reads directly on the instant claims.

#### **Applicants' Response**

The Examiner argues that Luciani I discloses a Ti/Mg molar ratio that can vary from 0.2 to 1 to 5 to 1, which if calculated, reads directly on the instant claims. However, lines 25 to 28 on page 2 of Luciani I do not refer to the molar ratio of Ti/Mg but rather to the molar ratio of titanium tetraalcoholate to magnesium chloride, that is, to a molar ratio of solutions. Furthermore, although the Examiner argued at the interview that he could calculate the amounts of catalyst components using the range of Ti/Mg solution from step (a) from Luciani I and step (ii) from Luciani II, this approach is not correct because the catalyst synthesis involves different kinds of unit operations, such as for example, filtration, decantation, multiple washes and the like which would make a calculation substantially impossible.

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